PB86-224565

Treatment Technologies for Hazardous Wastes
Part 3. Treatment Technologies for Corrosive Hazardous Wastes

(U.S.) Environmental Protection Agency
Cincinnati, OH

1986

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before complet

1. REPORT NO. EPA/600/J-86/108	2.	3. PB86-224565
4. TITLE AND SUBTITLE TREATMENT TECHNOLOGIES FOR HAZARDOUS WASTES: Part III. Treatment Technologies for Corrosive Hazardous Wastes. (Journal Version)		5. REPORT DATE 1986 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) H. Paul Warner and Robert A. Olexsey		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Hazardous Waste Engineering Research Laboratory USEPA Cincinnati, Ohio 45268		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. Inhouse
12. SPONSORING AGENCY NAME AND ADDRESS Hazardous Waste Engineering Research Laboratory USEPA Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Journal Article 14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES
REF: Journal of the Air Pollution Control Association, 36(4):403-409, April 1986

16. ABSTRACT

In this paper, the authors present generation and treatment information for corrosive hazardous wastes (EPA Hazardous Waste Codes D002 and K062). The authors discuss the state of the art for several treatment trains used to process specific types of corrosive waste. Treatment trains incorporate various unit processes selected from but not limited to the following: neutralization, filtration, carbon adsorption, biological oxidation, distillation, air flotation, and incineration. Unit processes are selected to form trains according to the corrosive characteristics of each individual waste stream. The treatment processes discussed are proposed to be used instead of landfills for disposal of corrosive waste.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to the Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 8
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA/600/J-86/108
JOURNAL ARTICLE

HAZARDOUS WASTE MANAGEMENT

TREATMENT TECHNOLOGIES FOR HAZARDOUS WASTES: PART III

Treatment Technologies for
Corrosive Hazardous Wastes

H. Paul Warner and Robert A. Olexsey
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio

In this paper, the authors present generation and treatment information for corrosive hazardous wastes (EPA Hazaradous Waste Codes D002 and K062). The authors discuss the state of the art for several treatment trains used to process specific types of corrosive waste. Treatment trains incorporate various unit processes selected from but not limited to the following: neutralization, filtration, carbon adsorption, biological oxidation, distillation, air flotation, and incineration. Unit processes are selected to form trains according to the corrosive characteristics of each individual waste stream. The treatment processes discussed are proposed to be used instead of landfills for disposal of corrosive waste.

A hazardous waste is characterized as a corrosive waste if it meets the following criteria:

1. It is aqueous and has a pH less than or equal to 2 or greater than or equal to 12.5.
2. It is a liquid and corrodes SAE 1020 steel at a rate greater than 6.35 mm (0.25 inch) per year at a test temperature of 55°C (130°F).[1]

Corrosive wastes, along with wastes containing metals and cyanides and halogenated organics comprise the "California List" wastes in that they are cited in regulations developed by the California Department of Health Services. The Hazardous and Solid Waste Amendments (HSWA) of 1984 require that the U.S. Environmental Protection Agency (EPA) decide by July 8, 1987 what restrictions to impose on the land disposal of the California List wastes. If EPA has not established treatment standards for corrosive wastes by that date, those wastes will be banned from land disposal.[2]

The purpose of this paper is to provide a summary review of commercially available treatment process technologies for various types of corrosive hazardous wastes. Applicability and limitations of each process for specific wastes are outlined with discussion.

Waste Characteristics and Generation

The wastes which are listed as corrosive wastes under the stipulations of the Resource Conservation and Recovery Act of 1976 (RCRA) have the following RCRA identification codes:

D002 A solid waste that exhibits the characteristic of corrosivity but is not listed as a hazardous waste in Subpart D of the RCRA regulations (waste is not an F, K, U, or P waste)

K062 Spent pickle liquor from steel finishing operations

The predominant source of generation of D002 wastes are the primary metals and metals finishing industries, with about 44 percent of the total. The chemicals industry is responsible for 27 percent followed by the utilities (8 percent) and petroleum (4 percent).

The statutory descriptions of corrosive wastes are specific to liquids. However, many of the wastes which are classified as D002 wastes contain solids and sludges.

While only two RCRA waste codes are listed as corrosive, these wastes are generated at substantial rates in the U.S. Data on waste generation for 1981 are shown in Table I. In addition, many of the wastes that are listed as metals or cyanide bearing wastes also exhibit the characteristic of corrosivity. For reference, total U.S. hazardous waste generation in 1981 was 240 billion gallons.

In 1981, about 3.4 billion gallons of hazardous corrosive wastes were disposed of to the land, with the largest amount, 3.0 billion gallons, going to deep well injections. Thirteen billion gallons were treated in tanks, surface impoundments, and incinerators. Simple storage accounted for about 8.4 billion gallons.[4] Treatment is conducted mainly on-site, that is, at the point of generation. Treatment, storage, and disposal quantities may exceed generation rates due to some double accounting; that is, some wastes which are both stored and treated are accounted for in both categories.

Treatment Objectives

The goal of any alternative hazardous waste treatment process is to render the waste harmless, nontoxic, and non-leachable into the groundwater. Liquid discharges must meet either National Pollutant Discharge Elimination System (NPDES) or Publicly Owned Treatment Works (POTW) pretreatment requirements.

A principal method for determining residue quality has been the Extraction Procedure Toxicity Characteristic

Copyright 1986-Air Pollution Control Association

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

Table I. Data on waste generation for 1981. Source: Reference 3.

Waste I.D.	Waste generation (millions of gallons)	Number of facilities
D002	19,916	513
K062	849	64

(EPTC). The toxicity characteristic entails use of a leaching test to measure the tendency of a waste to leach, coupled with extract concentrations above which the waste is defined to be a regulated, or hazardous waste. The current EPTC addresses only eight elements and six organic compounds. The Agency is currently developing an improved leaching test, the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP will address over 50 compounds and is expected to be more rugged and precise than the EPTC. The expanded TCLP will most likely be promulgated by EPA late in 1986.[5]

When the TCLP goes into effect, any waste, including a corrosive waste, must pass this test before it can be disposed of to the land. Therefore a key benchmark for any treatment process is the ability of the residue to pass the TCLP. If the residue does not pass the TCLP it must be subjected to further treatment until it passes the TCLP.

Treatment Technologies

The treatment technologies discussed here have been excerpted from a number of sources. The primary reference is a draft report to EPA by Camp Dresser and McKee, Inc., "Technical Assessment of Treatment Alternatives for Waste Containing Corrosives."[4]

There are essentially three technologies employed in the treatment of corrosive wastes. They are neutralization, resource recovery, and incineration. Neutralization is the most commonly applied treatment technique and will be discussed more extensively than the other technologies.

Simply stated, the process of neutralization is the interaction of an acid with a base. The typical properties exhibited by acids in solution are a result of the hydrogen ion concentration (H^+). Similarly, alkaline (or basic) properties are a result of the hydroxyl ion concentration (OH^-). In aqueous solutions, acidity and alkalinity are defined with respect to pH, where $pH = -\log (H^+)$, and $pH = 14 - \log (OH^-)$ (at room temperature), respectively. In the strict sense, neutralization is the adjustment of pH to 7, the level at which the concentrations of hydroxyl ion and hydrogen ion are equal. Solutions with excessive hydroxyl ion concentration ($pH > 7$) are said to be basic; solutions with excess hydrogen ions ($pH < 7$) are acidic. Since adjustment of pH to 7 is not often practical or even desirable in waste treatment, the term "neutralization" is sometimes used to describe adjustment of pH to values near neutrality.[6]

The first step to be taken in the treatment of corrosive wastes is treatment process selection. The appropriate applied treatment technology is dictated by the results of a corrosive waste characterization. This characterization will answer questions such as;

(a) Should the waste be neutralized?
(b) Does the waste contain chelated metals, cyanides or chromium?
(c) If the waste is neutralized, at what point in the treatment scheme should it be neutralized and with what neutralization agent?
(d) Are the wastes compatible with the neutralizing agent?
(e) What is the effect of the forma-

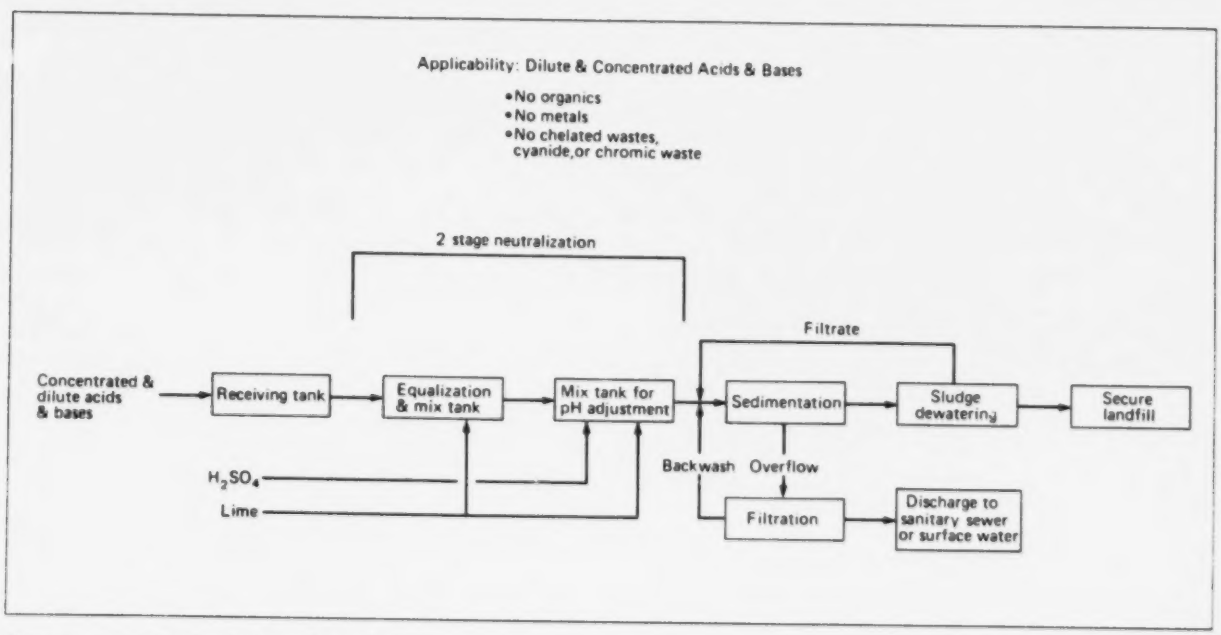

Figure 1. Aqueous treatment of inorganic wastes.

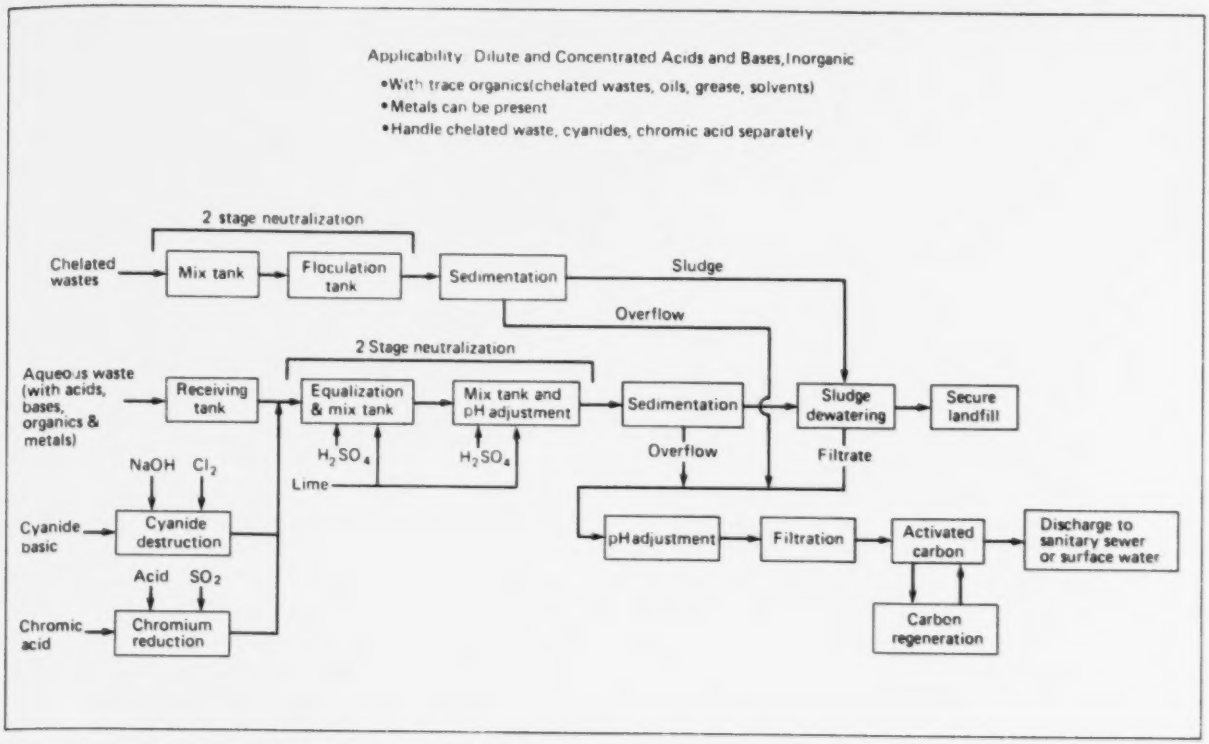

Figure 2. Aqueous treatment of wastes with metals and trace organics.

tion, if any, of soluble or insoluble salts?

(f) What are the downstream process effects?

Following an evaluation of the results of the physical and chemical characterization of the corrosive waste, a generic treatment process is selected and, when necessary, modified to incorporate specific techniques which must be applied to treat specific wastes.

In the treatment of corrosive wastes, the wastes are segregated to facilitate treatment as well as to avoid the mixing of incompatible wastes and the possibility of violent or dangerous reactions. Almost all generic treatment of corrosive waste incorporates neutralization prior to other treatment processes because highly acidic or basic wastes interfere with or cause failure of other downstream treatment processes such as biological treatment or carbon adsorption, and can cause severe corrosion problems if the waste comes in contact with downstream equipment.

The generic processes to be discussed are listed below:

A. Aqueous treatment of inorganic wastes.
B. Aqueous treatment of wastes with metals and trace organics.
C. Aqueous treatment of dilute organic wastes.
D. Recovery/reuse of halogenated and nonhalogenated solvents.
E. Incineration of combustible sludges, solids and liquids.
F. Treatment of heavy metal sludges.
G. Recovery and treatment of concentrated and dilute oils.

(A) Aqueous Treatment of Inorganic Wastes

The generic process for the aqueous treatment of inorganic wastes is presented in Figure 1. This process is applicable to dilute and concentrated acids and bases without metals, organics, cyanides, chelated wastes or chromic acid. The process consists of two-stage neutralization followed by a solid/liquid separation process. The first neutralization stage would control the pH within a rather broad range and the second would adjust the pH to a value between 6 and 9. The sludge generated from the formation of insoluble salts would be settled and further processed to remove water. A frequently employed dewatering unit is the filter press which can achieve cake solids of 40–50 percent. The dewatered solid would be subject to the Toxicity Characteristic Leaching Procedure (TCLP) test and, if passed and sufficiently low in moisture, could be disposed of in a secure landfill. The sedimentation effluent would be filtered to remove most of the remaining solids and then discharged to a municipal sewer or a surface water assuming effluent quality met applicable POTW or NPDES standards. Backwash from the filters would be recycled to the process feed or introduced prior to sedimentation.

(B) Aqueous Treatment of Wastes with Metals and Trace Organics

The treatment process for aqueous wastes with metals and trace organics is presented in Figure 2. This generic process is applicable to dilute and concentrated acids and bases containing metals in solution up to several thousand parts per million and trace organics at concentrations up to about 500 ppm. This treatment process is initially the same as the previously described process. However, the pH in first stage neutralization would have to be increased to 9.0 or more to precipitate the metals and the resultant sludge may not pass the TCLP test and be disposed of in a secure landfill but may

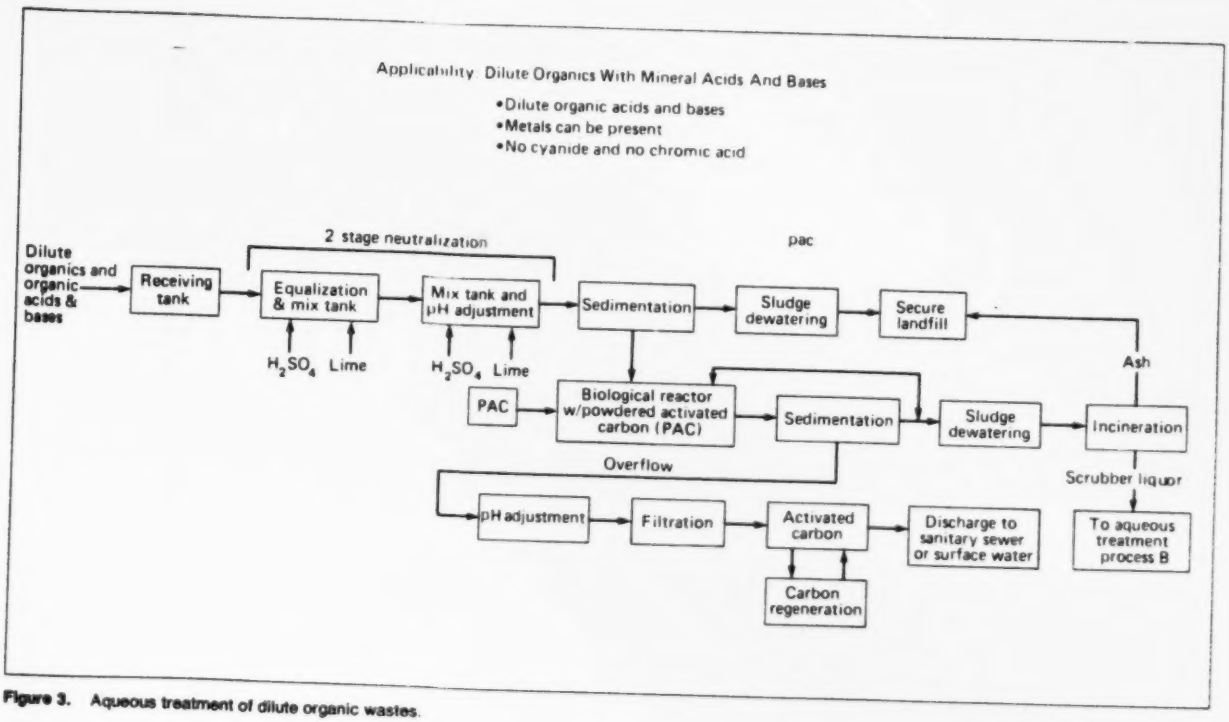

Figure 3. Aqueous treatment of dilute organic wastes.

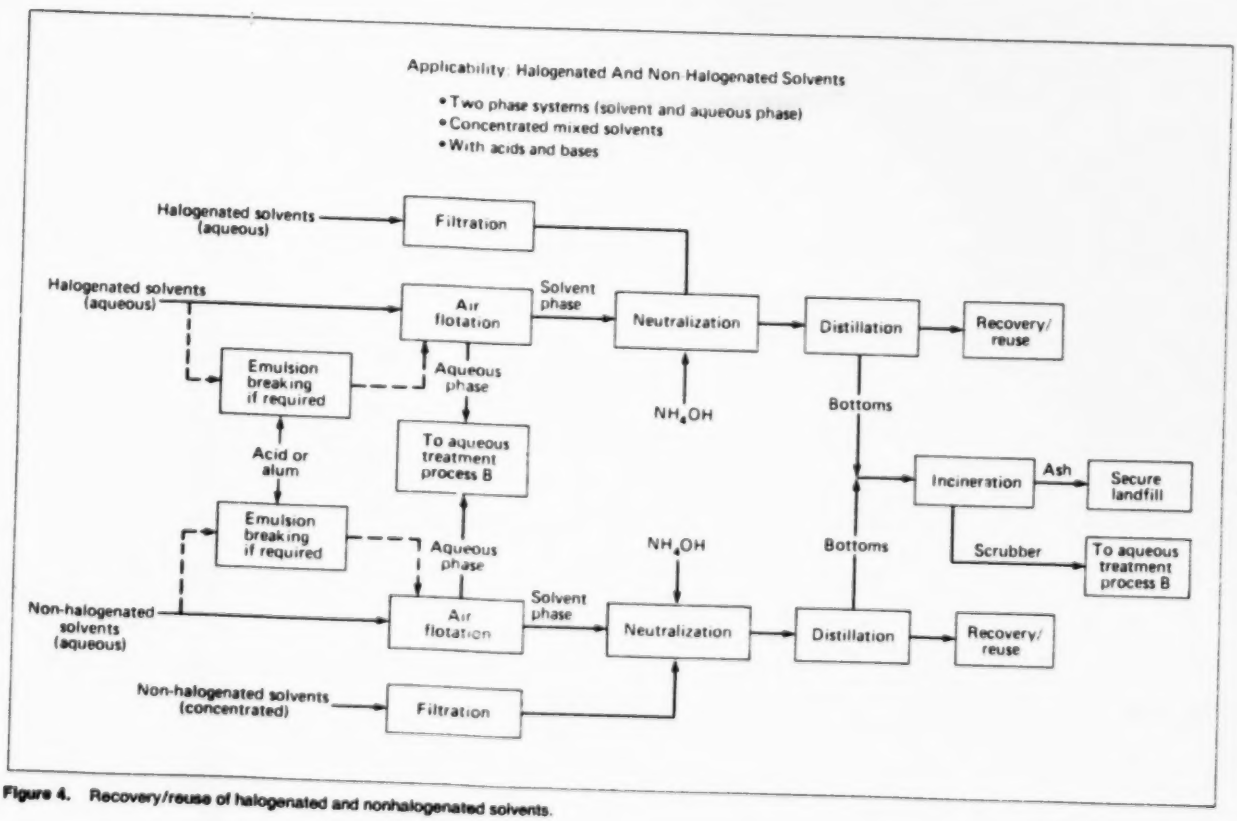

Figure 4. Recovery/reuse of halogenated and nonhalogenated solvents.

require further treatment such as stabilization/solidification. The effluent from the sedimentation tank due to organic and low level metal concentration would require further treatment. Prior to carbon adsorption for organic removal, the effluent from sedimentation must have the pH adjusted to about 7.0 and be filtered to remove remaining suspended solids. The spent carbon could be thermally regenerated and the carbon effluent could be discharged to a municipal sewer or to surface water.

If the corrosive feed contained cyanides, chromic acid, or chelated wastes, or if these wastes were blended with the feed, they would have to be treated separately and prior to Stage 1 neutralization.

Cyanide wastes should never be mixed with acid due to hydrogen cyanide formation, and should be treated by alkaline chlorination which oxidizes the cyanide to carbon dioxide and nitrogen gas.

Chromic acid waste contains hexavalent chromium which must be reduced to the trivalent form prior to precipitation. This reduction takes place at a pH of 2.0 with the addition of a reducing agent such as sulfur dioxide or sodium bisulfite.

Chelated wastes contain metals which are difficult to remove due to the presence of chelating agents which, through chemical bonding, keep the metals in solution. These wastes would probably require lime treatment at a higher pH and it may be necessary to reduce the pH and attempt to precipitate the metals with aluminum sulfate or polymers or a combination of aluminum sulfate and polymers. The sludge from this process, following dewatering, could be disposed of in a secure landfill, assuming passage of the TCLP, or stored for additional treatment.

(C) Aqueous Treatment of Dilute Organic Wastes

The treatment process for dilute organic wastes is presented in Figure 3. The process is applicable to the treatment of dilute organic wastes containing mineral or dilute organic acids and bases. Metals can be present, but cyanide wastes and/or chromic acid cannot. This process consists essentially of neutralization, biological oxidation with powdered activated carbon, filtration, and granular carbon adsorption. Neutralization is required in the first stage of this train primarily to prevent a microorganics kill in the biological reactor. In addition, if metals were present, they would be precipitated in the first stage. The biological/carbon reactor, with organic loadings of up to 1000 ppm would produce an effluent with organic concentrations of from 10 to 50 ppm. This effluent would be filtered to remove remaining suspended solids and then polished with granular carbon, and finally discharged to any surface water. The biological carbon sludge, containing toxic organics, would be incinerated, and the ash from incineration, if found nonhazardous, could be disposed of in a secure landfill

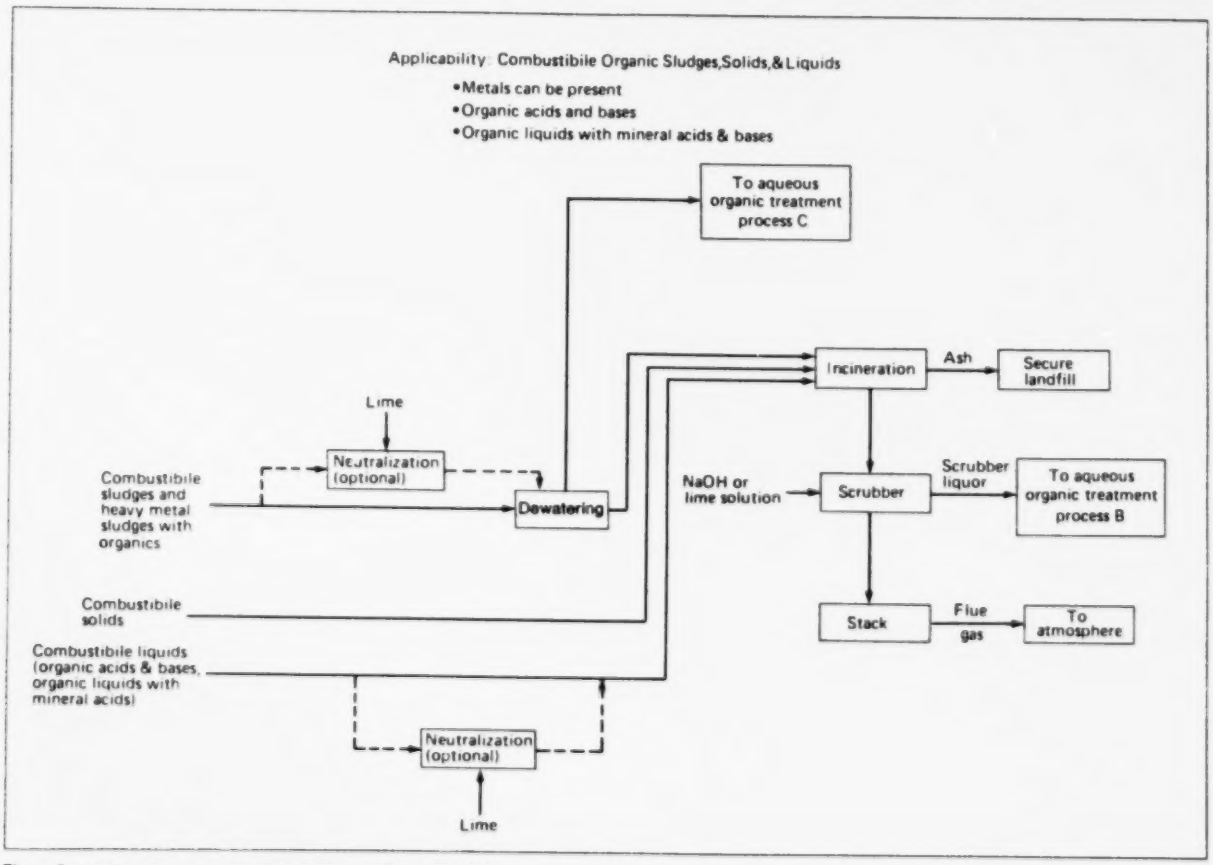

Figure 5. Incineration of combustible sludges, solids and liquids.

or, if found hazardous, could be treated by the stabilization/solidification process and then landfilled. The sludge from neutralization sedimentation would be handled as previously described.

(D) Recovery/Reuse of Halogenated and Nonhalogenated Solvents

The generic treatment process for recovery/reuse of halogenated and nonhalogenated solvents is presented in Figure 4. The process is applicable to dilute and concentrated solvents containing acids or bases. Halogenated solvents would be handled separately from nonhalogenated solvents. The dilute or aqueous streams would first go to an emulsion breaking process if required. The emulsion would be broken down by adding a highly ionized soluble salt of an acid, and once the emulsion is broken, the waste is separated into oil and aqueous phase by air flotation.

The aqueous phase would be piped to treatment process (B) for additional treatment. The solvent phase would be combined with the concentrated solvent and then neutralized.

The choice of the neutralizaton agent must be carefully considered in this instance. Lime is not recommended due to scaling problems in the distillation unit. Sodium based alkalis are not recommeded either due to the fact that they form eutectic solids in incineration and can cause serious ash fusion and clinkering problems. For this application ammonium hydroxide is the recommended neutralizing agent. The bottoms from the evaporation unit may be corrosive and may require incineration.

(E) Incineration of Combustible Sludges, Solids, and Liquids

The generic process for the incineration of combustible sludges, solids, and liquids is presented in Figure 5. This process is applicable to organic sludges, solids, and liquids containing inorganic acids and bases, and to inorganic acids and bases. Metals can be present in the waste stream. Neutralization prior to incineration is optional in this case provided the incinerator combustion chambers are lined with an acid resistant refractory or firebrick. The national survey data revealed six facilities which burn D002 corrosive waste. This neutralization option could also be considered in the previously described treatment scheme [process (D)].

Combustible solids would probably not be neutralized, since this would require addition of water to the waste stream, reducing its heating value. Combustible sludges would probably be dewatered in an acid resistant (if not neutralized prior to dewatering) filter press to 40–50 percent solids. The filtrate from the dewatering unit would be sent to generic process (C) for additional treatment.

A rotary kiln or fluidized bed incinerator would be suitable for handling most waste of this type. The fluid bed is an ideal combustor for liquids and pumpable solids, and would be acceptable for solids if they were reduced to a size of about 1–2 inches.

Flue gas from incineration would require scrubbing. The liquid would require further treatment and could be sent to generic process (B). The incineration ash may be hazardous and may require further treatment such as stabilization/solidification prior to disposal in a secure landfill.

(F) Treatment of Heavy Metal Sludges

The treatment process for heavy metal sludges is presented in Figure 6. The process is applicable to inorganic sludges containing metals, and inorganic and organic acids and bases. This process is similar to process (A) except a filter press is incorporated for solids

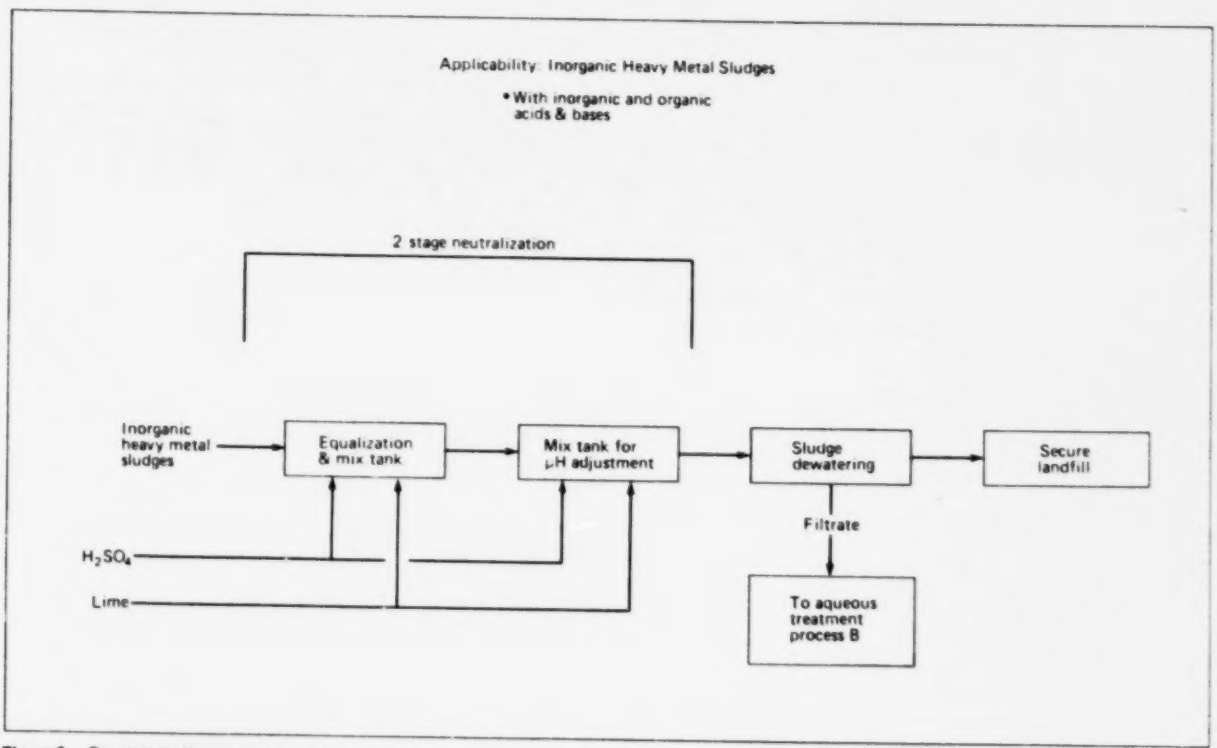

Figure 6. Treatment of heavy metal sludges.

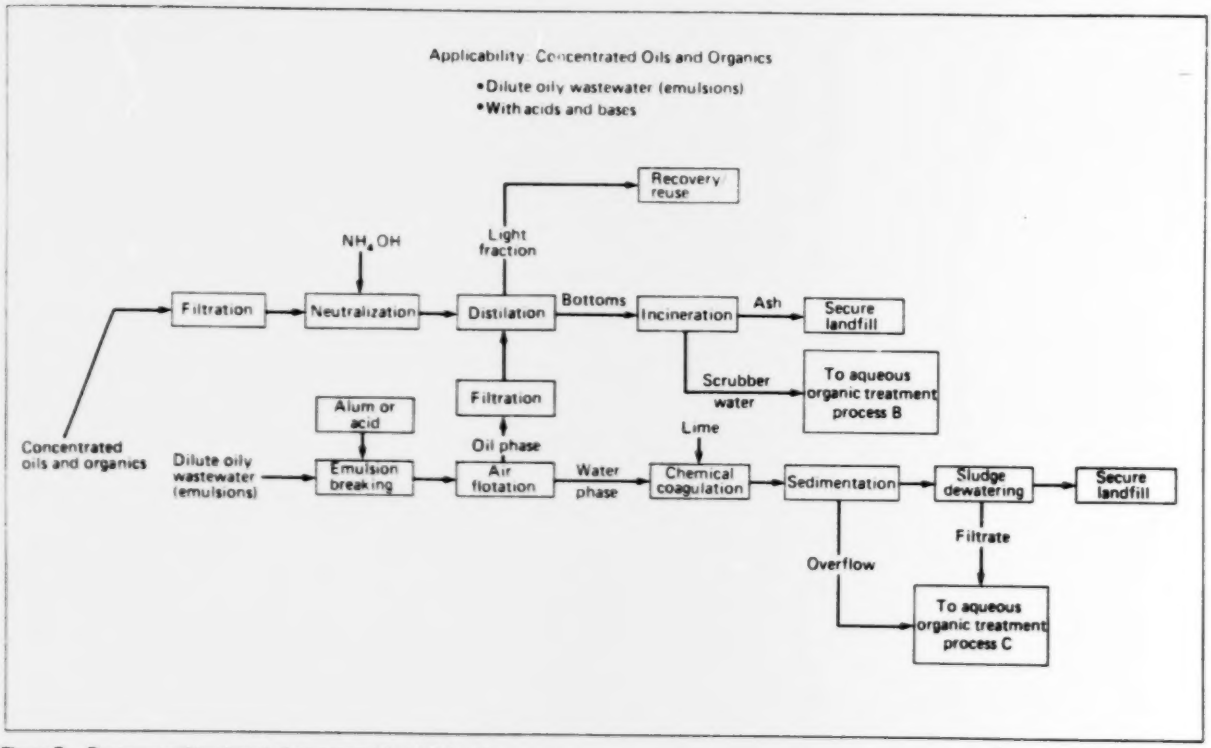

Figure 7. Recovery and treatment of concentrated and dilute oils.

separation rather than a sedimentation tank. The filtrate from the press would be piped to process (B) for additional treatment. If determined to be non-hazardous, as prescribed by the TCLP test, the filter cake could be disposed of in a secure landfill.

(G) Recovery and Treatment of Concentrated and Dilute Oils

The generic process for recovery and treatment of oils is presented in Figure 7. The process is applicable to concentrated and dilute oils and organic containing acids and bases. If emulsions are present, they would be broken down and then separated into the oil and aqueous phases in an air flotation unit. The oil in the aqueous phase would be chemically coagulated and then settled out of solution. The sludge would be dewatered and, if non-hazardous, disposed of in a secure landfill. The overflow from sedimentation would be sent to process (C) for additional treatment.

Concentrated oils and organics could be recovered by distillation, and the bottoms from the distillation tower could be incinerated. The waste would more than likely be neutralized with ammonium hydroxide prior to distillation.

Conclusions

Corrosive hazardous wastes are primarily liquid wastes and account for almost 12 percent of total annual hazardous waste generation in the U.S. Treatment technologies that can be used to treat corrosives are not complex but process selection is critical due to the impact of the waste material on treatment hardware. Post-neutralization residues may require further treatment such as fixation or incineration. The description of generic treatment processes presented here can be employed as screening mechanisms in treatment selection for specific corrosive wastes.

Acknowledgment

Special thanks are due Ernst Grossman III for his last minute efforts which enabled completion of the figures for this paper.

Notice. This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

1. *Federal Register*, 40 CFR Part 261, May 20, 1981.
2. S. E. Bromm, "USEPA's Land Disposal Restrictions Regulatory Programs," Proceedings of National Conference on Hazardous Wastes and Environmental Emergencies, Cincinnati, OH, May 1985.
3. "National Survey of Hazardous Waste Generators and Treatment, Storage, and Disposal Facilities Regulated under RCRA in 1981," Westat, Inc., report to U.S. EPA.
4. "Technical Assessment of Treatment Alternatives for Wastes Containing Corrosives," Camp Dresser and McKee, Inc., draft report to U.S. EPA, September 1984.
5. D. Friedman, "Development of an Organic Toxicity Characteristic for Identification of Hazardous Waste," U.S. EPA, Speech, Brussels, Belgium, September 1985.
6. *Treatability Manual—Volume III, Technologies for Control/Removal of Pollutants*, U.S. EPA, Office of Research and Development, September 1981.

H. Paul Warner and Robert A. Olexsey are with the Treatment Technology Staff, Thermal Destruction Branch, Alternative Technologies Division, Hazardous Waste Engineering Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH 45268. This technical paper was submitted for peer review in January 1986; the revised manuscript was received March 3, 1986.